

Photocatalytic Reduction, Reforming, and Oxidation Using TiO₂ from Aqueous Solution of Ethyl Violet Dye under Anaerobic Condition

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Abstract

The conversion of biomass into biogas is a form of “green energy” that has attracted particular attention. The production of biogas could provide solutions to two highly problematic concerns: the treatment of waste/wastewater and their conversion into a source of “clean energy”. One alternative to the traditional production of biogas through anaerobic digestion could be the generation of methane and other useful hydrocarbons via photocatalytic reduction. Photocatalysis is considered non-specific for particular substances, making it applicable to any type of substrates, even those that are toxic to bacteria. In this study, we investigated the photocatalytic reactions of an aqueous solution of ethyl violet (EV) over TiO₂, in which BTEX (benzene, toluene, ethylbenzene, and xylene), ethane, and diethylamine were found by Headspace-GC-MS and mono-, di-, tri-, tetra-, penta-, and hexa-*N*-de-methylated CV species and 4-dimethylaminophenol, 4-dimethylamino-4'-dimethylaminobenzophenone and their *N*-de-methylated products were detected by HPLC-PDA-ESI-MS. Photocatalytic reduction (PCR) and photocatalytic reforming (PR) appear to play an important role in the generation of BTEX. The PCR and PR of EV for the production of BTEX have never been studied. It is our belief that a deeper understanding of the mechanism could be beneficial to the preparation of photocatalysts and the production of BTEX using the photocatalytic process. Based on our results, we propose a possible mechanism to explain the photocatalytic process.

Keywords: Photocatalytic Reduction, Reforming, BTEX, TiO₂, Ethyl Violet

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1 Introduction

Photocatalytic oxidation (PCO) of wastewater containing toxic organic compounds using TiO₂ has been extensively studied in recent years [1,2]. The ultimate objective of PCO is to convert the organic substrates to H₂O and CO₂. Recently, with mounting concerns over climate change and the depletion of fossil fuels, there has been a revived interest in the production of H₂ by photocatalytic decomposition of organic substances [3]. These substances include biomass and its derivatives [4], such as cellulose, starch, sucrose, glucose, and glycerol, alcohols such as methanol, ethanol and C3-polyols [5,6]. The reaction condition is almost the same as that of PCO but without bubbling O₂ or air to suppress the thermal back-reaction of H₂ with O₂. H₂O, instead of O₂, was used as oxidant to split organic compounds to H₂ and CO₂. The H₂ evolution rates were generally much higher than that of splitting pure water because of the presence of organic substances. As the process is analogous to the catalytic thermal reforming process, it was commonly called photocatalytic reforming (PR) reaction. Obviously, the reaction not only involves the decomposition and mineralization of organic substrates, but also involves the splitting of water to produce H₂. PR of C3-polyols and glucose for H₂ production over noble-metal-loaded TiO₂ has been investigated by Wang *et al.* [6,7].

The depletion of non-renewable resources of fossil fuels and the necessity of the reduction of their negative impact on the environment have recently become an important issue. In view of this, there is a great demand for the development of new environmentally friendly methods of energy production. Amongst different conceptions of production of “green energy” a conversion of biomass into biogas is the one that

attracts particular attention [8]. Biogas production could be a solution for the two very problematic concerns: treatment of waste or wastewater and their conversion into “clean energy.”

An alternative to the traditional anaerobic digestion method of biogas production could be generation of methane and other useful hydrocarbons via photocatalytic reduction (PCR) [9]. Photocatalysis is considered as not specific for particular substances [10], therefore it could be applied for any types of substrates, even those, which are toxic to bacteria. This enhances the competitiveness of photocatalysis in the discussed application.

The photocatalytic generation of $C_1 - C_3$ hydrocarbons and hydrogen from aqueous solution of acetic acid over TiO_2 has been investigated by Mozia *et al.* [11]. Acetic acid undergoes the photo-Kolbe reaction yielding CH_4 and CO_2 . Therefore, the gaseous mixture obtained during the photocatalytic reaction has a similar composition to that of biogas produced by a conventional anaerobic digestion method.

PCO of Ethyl Violet (EV) for mineralization over TiO_2 has been investigated in our former work [12]. In this work, we noticed that the photocatalytic generation of BTEX, ethane, and diethylamine from aqueous solution of EV over TiO_2 . The photocatalytic reduction and reforming seemed playing an important role in generation of benzene, toluene, ethylbenzene, and xylene (BTEX). Although PCR and PR of EV for BTEX production have been never studied, little work has been attempted to elucidate the reaction mechanism owing to the difficulty in applying HPLC-MS and GC-MS techniques in these suspension systems. However, they may still offer some useful insights for the understanding of the PR reaction if the measurement is taken under conditions close to the real reforming system. This proposition is further supported by the present experimental work. We believe a better understanding of the reforming mechanism will benefit both the photocatalyst preparation and the BTEX production reaction by the PR process. According to the results, a possible mechanism for the process was suggested and discussed.

2 Experimental

2.1 Materials and Reagents

The P25 TiO_2 nanoparticles were supplied by Degussa. Standards of the following compounds were used: benzene (99%), toluene (99%), o-xylene (99%), m-xylene (99%), p-xylene (99%), and ethylbenzene (99%) from Acros. 1,4-difluorobenzene (Merck), and EV dye (TCI) were obtained and used without any further purification.

2.2 Instruments and Analytic methods

Headspace-GC-MS system, equipped with a AutoSystem XL Gas Chromatograph, a PerkinElmer TurboMass Gold Mass Spectrometer, and Turbomatrix 40 Headspace Samplers. Waters ZQ LC/MS system was used to identify the reaction intermediates.

2.3 Photocatalytic reaction

An aqueous TiO_2 dispersion was prepared by adding 100 mg of TiO_2 powder into a 10 mL solution containing the EV at appropriate concentration. The results obtained are more likely different from that of PCO of EV over TiO_2 under a N_2 condition, i.e. O_2 free condition. Therefore, to study the reforming mechanism, it is essential to conduct a separate GC-MS and HPLC-MS measurement.

3 Results and Discussion

3.1 GC-MS Analysis

To investigate the PR process of these systems in situ in real-time is still impossible.

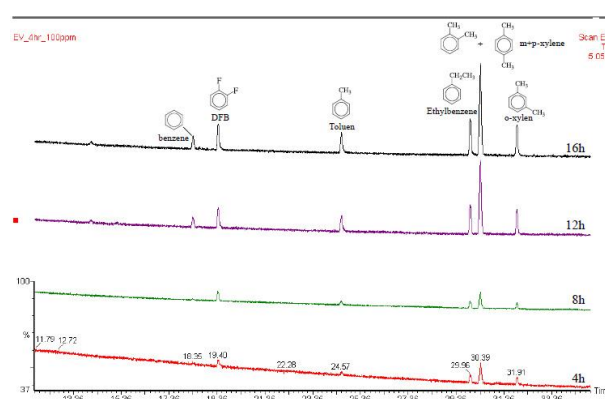


Figure 1: Variation in the relative distribution of the products obtained from the photocatalytic reduction of EV as a function of irradiation time.

A relatively feasible way at present is to use GC-MS and HPLC-MS for it can identify both the PCO and PCR intermediates (both liquid- and gas-phase intermediates)

although its reaction conditions are not exactly as the real reforming reaction. The intermediates were marked in the GC chromatograms (**Figure 1**) and the relevant mass spectra

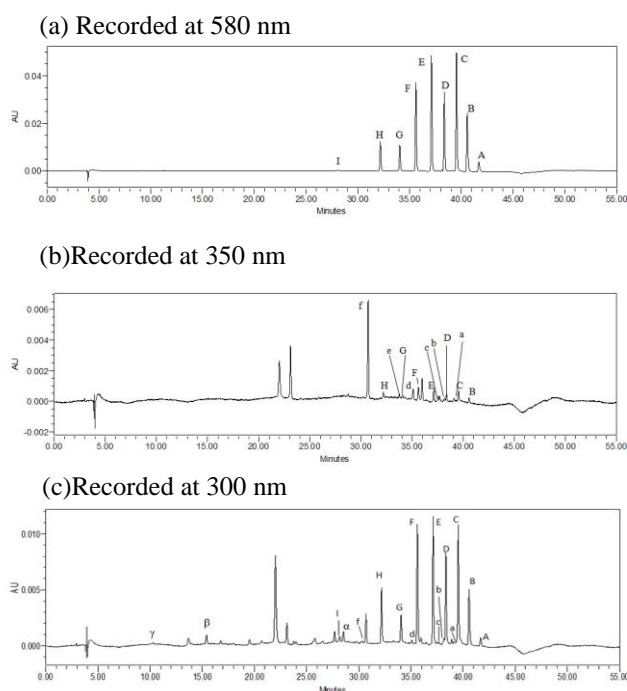


Figure 2: HPLC chromatogram of the intermediates with TiO_2 0.01 g, at pH 6, at 8 h of irradiation, recorded at (a) 580 nm, (b) 350 nm, and (c) 300 nm.

are illustrated in **Table 1**. Up to six compounds could be detected as possible degradation intermediates in **Figure 1**. We denoted these intermediates as compounds **BTEX**.

3.2 HPLC-PDA-ESI-MS Analysis

Temporal variations occurring in the solution of EV dye during the degradation process with UV irradiation were examined using HPLC coupled with a photodiode array detector and ESI mass spectrometry. The chromatograms at pH 6 are illustrated in **Figure 2**, recorded at 580, 350, and 300 nm. Eighteen components were identified, all with retention time of less than 55 min. We denoted the EV dye and its related intermediates as species A-I, a-f, and α - γ . Except for the initial EV dye (peak A), the other peaks initially increased before subsequently decreasing, indicating formation and transformation of the intermediates. The *N*-de-ethylation of the EV dye has the wavelength position of its major absorption band moved toward the blue region. The oxidative degradation yields 4-diethylaminophenol (DAP), 4-diethylamino-4'-diethyl-

aminobenzophenone (DDBP), and their *N*-de-ethylated products. The *N*-de-ethylation of the DDBP, produced by cleavage of the EV chromophore ring structure, has the wavelength position of its major absorption band moved toward the blue region. The photodegraded intermediates were further identified using the HPLC-ESI mass spectrometric method. The molecular ion peaks appeared in the acid forms of the intermediates. Results of HPLC-ESI mass spectra are summarized in **Table 1**.

3.3 Photodegradation mechanisms of EV

3.3.1 Photocatalytic reduction and reforming

In PCO reaction, holes (h^+), hydroxyl radicals ($\cdot\text{OH}$) and superoxide anion radicals ($\text{O}_2^{\cdot-}$) are commonly suggested as the primary oxidizing species [12]. For our photocatalytic reaction, $\cdot\text{OH}$ are formed on TiO_2 surface by reaction of h^+ with OH^- or absorbed H_2O while $\text{O}_2^{\cdot-}$ won't originate from the reduction of O_2 by the photogenerated electrons (e^-). The primary difference between the PCO and the PR is that the former was performed under aerobic conditions, but the latter under anaerobic conditions. Thus, the formation of $\text{O}_2^{\cdot-}$ was avoided. h^+ and $\cdot\text{OH}$ become the main oxidants to attack the substrate of EV. Photogenerated electrons become the main reductants to attack the EV dye and its decomposed products. Based on these data, the PR mechanism of EV was finally discussed and proposed in **Figure 3**.

3.3.2 *N*-de-ethylation of EV

According to earlier reports [12-14], most *N*-de-alkylation processes are preceded by the formation of a nitrogen-centered radical while destruction of dye chromophore structures is preceded by the generation of a carbon-centered radical. Consistent with this, degradation of EV must occur via two different photodegradation pathways (destruction of the chromophore structure and *N*-de-ethylation) due to formation of different radicals (either a carbon-centered or nitrogen-centered radical). There is no doubt that the $\cdot\text{OH}$ attack on the dye yields a dye cationic radical. After this step, the cationic radical $\text{Dye}^{+\cdot}$ can undergo hydrolysis and/or follow various deprotonation pathways, which in turn are determined by the different adsorption modes of EV on the TiO_2 particles surface.

On the basis of all the above experimental results, we tentatively propose the pathway of photodegradation

depicted in **Figure 4**. In this Figure, the dye molecule in the EV/TiO₂ system is adsorbed through the positively charged diethylamine function. Following one [•]OH radical attracted a hydrogen atom from ethyl group of diethylamine, and another [•]OH radical attacked the diethylamine radical and formed hydroxyethylated intermediates, the subsequent hydrolysis (or deprotonation) of intermediates yields de-hydroxyethylated intermediates, which were subsequently attacked by [•]OH radicals to lead ultimately to *N*-de-ethylation. The mono-de-ethylated dye derivative, DDMPR, can also be adsorbed on TiO₂ particle surface and be implicated in other similar events ([•]OH radicals attraction and attack, hydrolysis or deprotonation) to yield a bi-de-ethylated dye derivatives, DDPH and DMMPR. The *N*-de-ethylation process as described above continues until formation of the completely de-ethylated dye, PR.

3.3.3 Oxidative degradation of the EV

In the **Figure 4**, the dye molecule in the EV/TiO₂ system is adsorbed through a conjugated structure cleavage of the EV chromophore structure. Following [•]OH radical attack the conjugated structure yields a carbon-centered radical, which is subsequently attacked by molecular oxygen to lead

ultimately to DDBP and DAP. The same process happened in the *N*-de-ethylated dye to produce the *N*-de-ethylated DDBP and DAP. The DDBP can also be adsorbed on the TiO₂ particle surface and be implicated in other similar events ([•]OH radical attraction and attack, hydrolysis or deprotonation, and/or oxygen attack) to yield a mono-*N*-de-ethylated derivative, DEBP. Moreover, the same process happened in DAP to produce EAP. The *N*-de-ethylation process as described above continues until formation of the completely *N*-de-ethylated DDBP, BP, and *N*-de-ethylated DAP, AP. All the above *N*-de-ethylation processes produced a series of *N*-de-hydroxyethylated intermediates by the hydroxylation on the *N*-ethyl group. All the intermediates were further degraded to produce *N,N*-diethylaminobenzene, *N*-ethylaminobenzene, amino-benzene, acetamide, 2-propenoic acid, and acetic acid, which were subsequently mineralized to lead to CO₃²⁻ and NO₃⁻ [12-15].

On the basis of all the above experimental results, we tentatively propose the pathway of photodegradation depicted in **Figure 5**. PCR, PR, and PCO of EV take place in the presence of TiO₂ particles.

Table 1 :Identification of the intermediates from the photodegradation of EV by HPLC-ESI-MS or GC-EI-MS

HPLC peaks	Intermediates	Abbreviation	MS peaks (m/z)	Absorption maximum (nm)
A	<i>N,N,N',N',N'',N''</i> -hexaethylpararosaniline	EV	456.51	592.2
B	<i>N,N</i> -diethyl- <i>N',N'</i> -diethyl- <i>N''</i> -ethylpararosaniline	DDEPR	428.48	584.9
C	<i>N,N</i> -diethyl- <i>N'</i> -ethyl- <i>N''</i> -ethylpararosaniline	DEEPR	400.46	583.6
D	<i>N,N</i> -diethyl- <i>N',N'</i> -diethylpararosaniline	DDPR	400.52	584.4
E	<i>N</i> -ethyl- <i>N'</i> -ethyl- <i>N''</i> -ethyl pararosaniline	EEPR	372.44	580.5
F	<i>N,N</i> -diethyl- <i>N'</i> -ethylpararosaniline	DEPR	372.37	581.5
G	<i>N</i> -ethyl- <i>N'</i> -ethylpararosaniline	EEPR	344.41	570.2
H	<i>N,N</i> -diethylpararosaniline	DPR	344.41	570.5
I	<i>N</i> -ethylpararosaniline	EPR	316.39	544.5
a	4-(<i>N,N</i> -diethylamino)-4'-(<i>N',N'</i> -diethyl amino)benzophenone	DDBP	325.41	379.5
b	4-(<i>N,N</i> -diethylamino)-4'-(<i>N'</i> -ethylamino)benzophenone	DEBP	297.38	373.1
c	4-(<i>N</i> -ethylamino)-4'-(<i>N'</i> -ethylamino)benzophenone	EEBP	269.29	365.5
d	4-(<i>N,N</i> -diethylamino)-4'-aminobenzophenone	DBP	269.29	372.1
e	4-(<i>N</i> -ethylamino)-4'-aminobenzophenone	EBP	241.33	357.2
f	4,4'-bis-aminobenzophenone	BP	213.17	344.2
α	4-(<i>N,N</i> -diethylamino)phenol	DAP	166.21	305.7
β	4-(<i>N</i> -ethylamino)phenol	EAP	N/A	289.2
γ	4-aminophenol	AP	N/A	281.9
	Benzene	BZ	78.11	N/A
	Toluene	TOL	92.14	N/A
	Ethyl benzene	EB	106.16	N/A
	Xylene	DMB	106.17	N/A

The BTEX intermediates were identified by GC-MS and the other intermediates were identified by HPLC-MS.

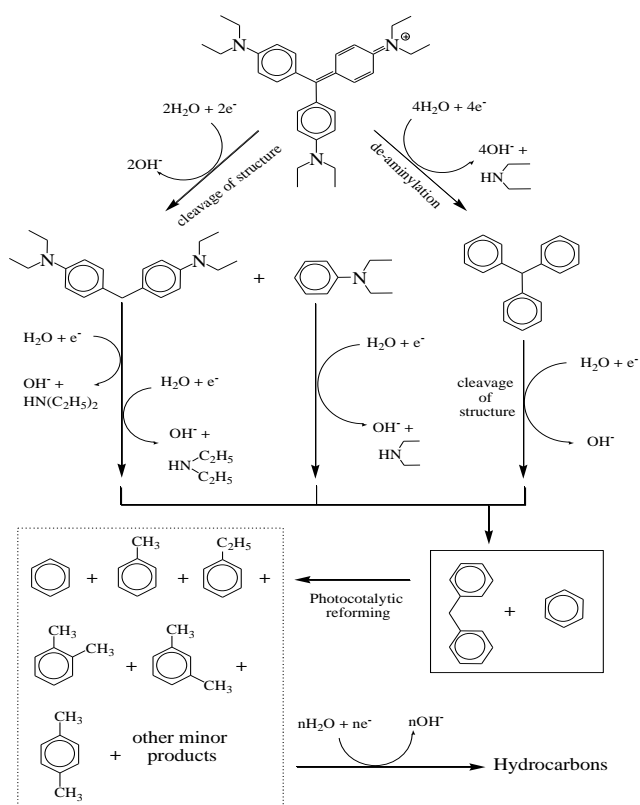


Figure 3: Mechanisms of photocatalytic reduction and reforming.

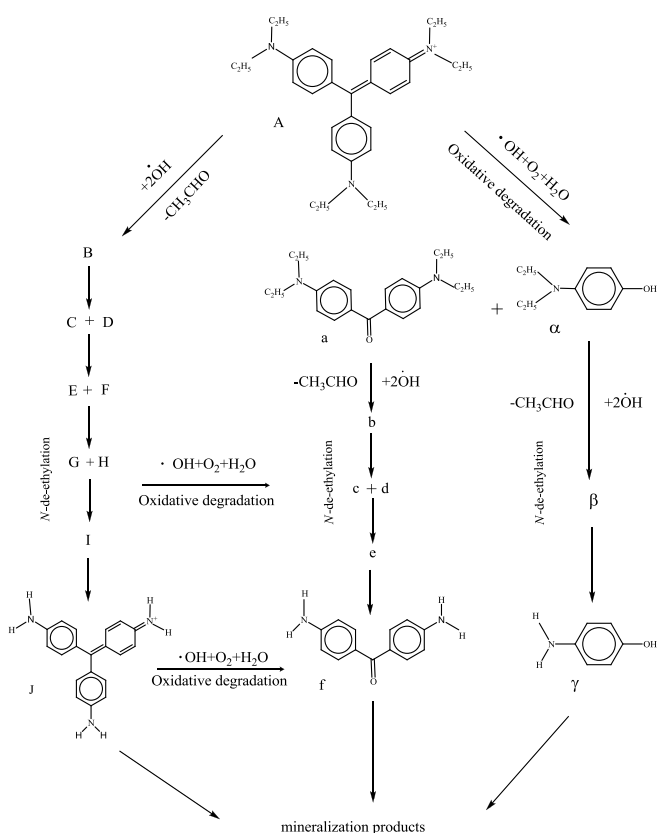


Figure 4: Proposed photodegradation pathways of the EV dye under UV irradiation in aqueous TiO_2 dispersions followed by the identification of several intermediates by HPLC-ESI mass spectral techniques.

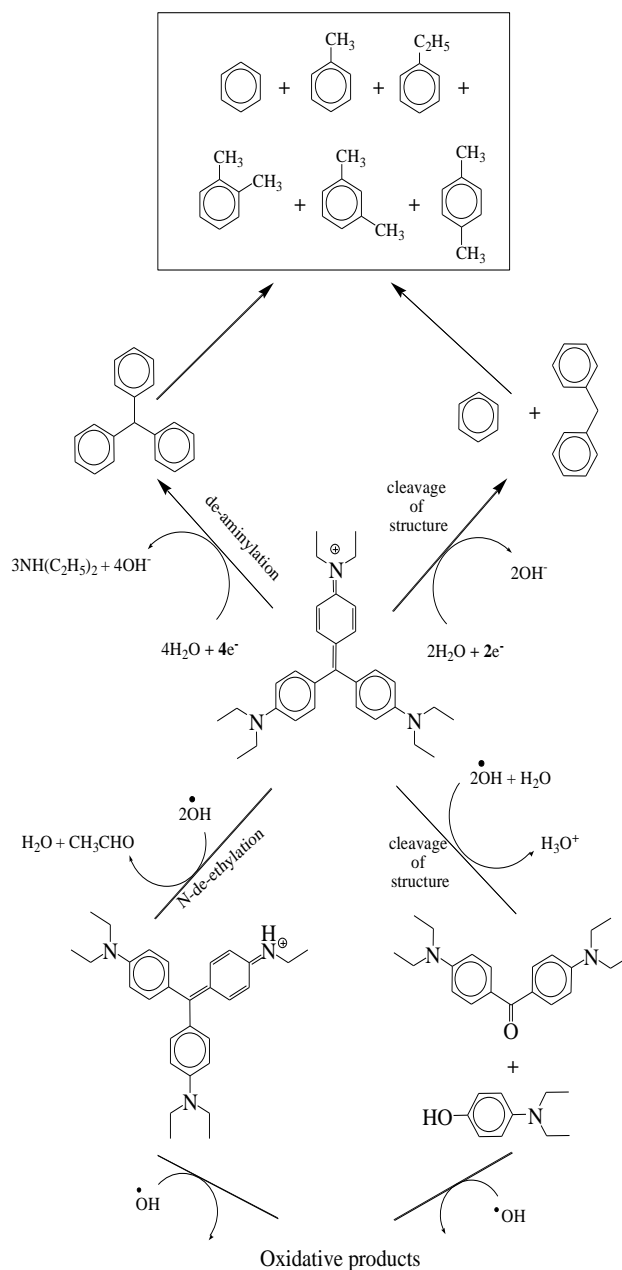


Figure 5: Mechanisms of photocatalytic degradation under anaerobic conditions.

4 Conclusion

Its intermediates in the process were subsequently explored. The results not only provide evidences for the study of EV, but also enhance our further understanding on photocatalytic degradation under anaerobic conditions. Based on these data, the degraded mechanism of EV was discussed and proposed. Both PCR and PCO of EV take place in the presence of TiO_2 particles. We believe a better understanding of the reforming mechanism will benefit both the photocatalyst preparation and the BTEX production reaction by the photocatalytic reduction process.

Acknowledgments

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References

- [1] M.R. Hoffmann, S.T. Martin, W.Y. Choi, D.W. Bahnemann. "Environmental Application of Semiconductor Photocatalysis", *Chem. Rev.* **95**, pp. 69-96, 1995.
- [2] A. Fujishima, T.N. Rao, D.A. Tryk, "Titanium dioxide photocatalysis", *J. Photochem. Photobiol. C*, **1**, pp.1-21, 2000.
- [3] (a) M. Bowker, D. James, P. Stone, R. Bennett, N. Perkins, L. Millard, J. Greaves, A. Dickinson. "Catalysis at the metal-support interface: exemplified by the photocatalytic reforming of methanol on Pd/TiO₂", *J. Catal.*, **217**, pp. 427-433, 2003. (b) X. Fu, X. Wang, D.Y.C. Leung, Q. Gu, S. Chen, H. Huang. "Photocatalytic reforming of C3-polyols for H₂ production :Part (I). Role of their OH groups ", *Appl. Catal. B: Environ.*, **106**, pp.681-688, 2011.
- [4] M. Bowker, P.R. Davies, L.S. Al-Mazroai. "Photocatalytic reforming of glycerol over gold and palladium as an alternative fuel source ", *Appl. Catal. B: Environ.*, **128**, pp.253-255, 2009.
- [5] G.L. Chiarello, D. Ferri, E. Selli. "Effect of the CH₃OH /H₂O ratio on the mechanism of the gas-phase photocatalytic reforming of methanol on noble metal-modified TiO₂", *J. Catal.*, **280**, pp.168-177, 2011.
- [6] Q. Gao, X. Fu, X. Wang, S. Chen, D.Y.C. Leung, X. Xie. "Photocatalytic reforming of C3-polyols for H₂ production :Part II . FTIR study on the adsorption and photocatalytic reforming reaction of 2-propanol on Pt/TiO₂", *Appl. Catal. B: Environ.*, **106**, pp.689-696, 2011.
- [7] X. Fu, J. Long, X. Wang, D.Y.C. Leung, Z. Ding, L. Wu, Z. Zhang, Z. Li. "Photocatalytic reforming of biomass: A systematic study of hydrogen evolution from glucose solution ", *Int. J. Hydrogen Energy*, **33**, pp.6484-6491, 2008.
- [8] Y. Santosh, T.R. Sreekrishnan, A. Kohli, V. Rana. "Enhancement of biogas production from solid substrates using different techniques – a review", *Bioresour. Technol.*, **95**, pp.1-10, 2004.
- [9] (a) S.C. Roy, O.K. Varghese, M. Paulose, C.A. Grimes. "Toward solar fuels: photocatalytic conversion of carbon dioxide to hydrocarbons", *ACS Nano*, **4**, pp. 1259-1278, 2010. (b) N.M. Dimitrijevic, B.K. Vijayan, O.G. Poluektov, T. Rajh, K.A. Gray, H. He, P. Zapol. "Role of water and carbonates in photocatalytic transformation of CO₂ to CH₄ on Titania", *J. Am. Chem. Soc.*, **133**, pp. 3964-3971, 2011.
- [10] V. Augugliaro, M. Litter, L. Palmisano, J. Soria. "The combination of heterogeneous photocatalysis with chemical and physical operations : a tool for improving the photoprocess performance ", *J. Photochem. Photobiol. C*, **7**, pp. 127-144, 2006.
- [11] S. Mozia, A. Heciak, A.W. Morawski. "The influence of physic-chemical properties of TiO₂ on photocatalytic generation of C₁-C₃ hydrocarbons and hydrogen from aqueous solution of acetic acid ", *Appl. Catal. B: Environ.*, **104**, pp. 21-29, 2011.
- [12] C.C. Chen, C.S. Lu. "Photocatalytic degradation of Basic Violet 4: degradation efficiency, product distribution, and mechanisms", *J. Phys. Chem. C*, **111**, pp. 13922-13932, 2007.
- [13] Y. H. Liao, J. X. Wang, J.S. Lin, W.H. Chung, W.Y. Lin, C.C. Chen. "Synthesis photocatalytic activities and degradation mechanism of Bi₂WO₆ toward crystal violet dye", *Catal. Today*, **174**, pp. 148-159, 2011.
- [14] H. Fan, C. Lu, J. Jan, M. Chiou, C.C. Chen. "Comparing Differences of Degradation Pathways between P25-TiO₂ and Pt-TiO₂ Mediated Photocatalysis under UV Irradiation", *J. Hazard. Mater.*, **185**, pp. 227-235, 2011.
- [15] A.B. Prevot, C. Baiocchi, M.C. Brussino, E. Pramauro, P. Savarino, V. Augugliaro, G. Marci, L. Palmisano. "Photocatalytic degradation of acid blue 80 in aqueous solutions containing TiO₂ suspensions", *Environ. Sci. Technol.* **35**, pp. 971-976, 2001.